

(19)



Europäisches Patentamt

Eur pean Pat nt Office

Office européen des brevets



(11)

EP 0 708 140 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

24.04.1996 Bulletin 1996/17

(51) Int. Cl.⁶: C08K 5/18, C08L 27/12

(21) Application number: 95116112.4

(22) Date of filing: 12.10.1995

(84) Designated Contracting States:
DE GB IT

(30) Priority: 21.10.1994 JP 282940/94

(71) Applicants:

- NIPPON MEKTRON, LTD.
Minato-ku Tokyo (JP)
- The Central Synthetic Rubbers Research
Institute named for S.V. Lebedev
198035 Saint Petersburg (RU)

(72) Inventors:

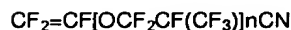
- Yamamoto, Yuichi
Takahagi City, Ibaraki (JP)

- Tatsu, Haruyoshi
Hitachi city, Ibaraki (JP)
- Alexeevna, Volkova Margarita
194017 Saint Petersburg (RU)
- Vasilyevich, Sokolov Sergey
198217 Saint Petersburg (RU)
- Vladimirovich, Veretennikov Nikolai
197341 Saint Petersburg (RU)

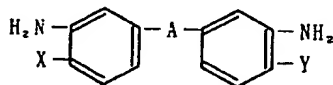
(74) Representative: Hansen, Bernd, Dr. Dipl.-Chem. et al
Hoffmann, Eitle & Partner,
Patentanwälte,
Arabellastrasse 4
D-81925 München (DE)

(54) Fluorine-containing elastomer composition

(57) A fluorine-containing elastomer composition, which comprises a terpolymer of tetrafluoroethylene, perfluoro(lower alkyl vinyl ether) and cyano group-containing (perfluorovinylether) represented by the following general formula:



, wherein n is an integer of 1 to 5, and a bis(aminophenyl) compound represented by the following general formula as a cross-linking agent:



, wherein A is, for example, an alkylidene group, and X and Y are a hydroxyl group or an amino group, can produce vulcanized products having a good heat resistance and good physical properties, and the bis(aminophenyl) compound has no problem as to its safety.

EP 0 708 140 A1

Description

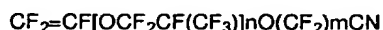
BACKGROUND OF THE INVENTION

1. FIELD OF THE INVENTION

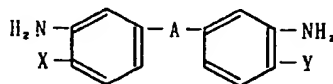
The present invention relates to a fluorine-containing elastomer composition, and more particularly to a cross-linkable composition of fluorine-containing elastomer having cyano groups as cross-linkable groups.

2. RELATED PRIOR ART

JP-A-59-109546 discloses a fluorine-containing elastomer composition which comprises a terpolymer of tetrafluoroethylene, perfluoro(methyl vinyl ether) and cyano group-containing (perfluorovinylether) represented by the following general formula:



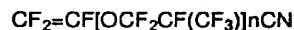
wherein n: 1-2 and m: 1-4
and a bis(aminophenyl) compound represented by the following general formula as a cross-linking agent:



wherein A is an alkylidene group having 1 to 6 carbon atoms, a perfluoroalkylidene group having 1 to 10 carbon atoms, a SO₂ group, an O group, a CO group or a carbon-carbon bond capable of directly bonding two benzene rings, and X and Y are hydroxyl groups or amino groups.

However, the cyano group-containing (perfluorovinylether), copolymerized as the cross-linking site monomer in the terpolymer, is synthesized through many steps, as disclosed in US Patent No. 4, 138, 426 and thus is never regarded as an industrially advantageous raw material.

On the other hand, US Patent No. 3,933,767 discloses a terpolymer of tetrafluoroethylene, perfluoro(methyl vinyl ether) and cyano group-containing (perfluorovinylether) represented by the following general formula as a cross-linking site monomer:



(wherein n: 1-5)

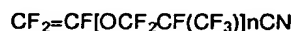
and also discloses that the cross-linking can be carried out with tetraphenyl tin.

The cyano group-containing (perfluorovinylether) used as the comonomer component for the terpolymer can be readily synthesized from the corresponding $\text{CN}[\text{CF}(\text{CF}_3)\text{CF}_2\text{O}]_n\text{CF}(\text{CF}_3)\text{COF}$ with a good selectivity, but the cross-linking of the thus obtained terpolymer is carried out with highly toxic tetraphenyl tin, and thus there are still problems of industrial safety and slow cross-linking speed. Furthermore, the thus obtained cross-linked products have less resistances to water and to amine at an elevated temperature.

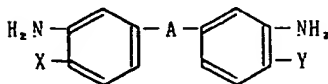
SUMMARY OF THE INVENTION

An object of the present invention is to provide a fluorine-containing elastomer composition capable of producing vulcanized rubber products having a good heat resistance and good physical properties with a commercially available, ordinary cross-linking agent free from any safety problem, as contained therein, the composition comprising a cross-linking site monomer which can be readily synthesized with a good selectivity.

According to the present invention, there is provided a fluorine-containing elastomer composition, which comprises a terpolymer of tetrafluoroethylene, perfluoro(lower alkyl vinyl ether) and a cyano group-containing (perfluorovinylether) represented by the following general formula:



, wherein n is an integer of 1 to 5 and a bis(aminophenyl) compound represented by the following general formula as a cross-linking agent:

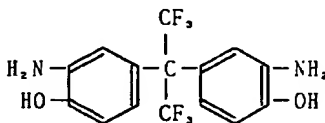


, wherein A is an alkylidene group having 1 to 6 carbon atoms, a perfluoroalkylidene group having 1 to 10 carbon atoms, a SO₂ group, an O group, a CO group or a carbon-carbon bond of directly combined two benzene rings, and X and Y are a hydroxyl group or an amino group.

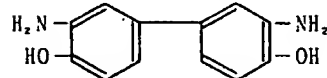
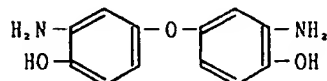
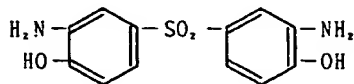
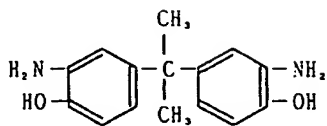
DETAILED DESCRIPTION OF THE INVENTION

The terpolymer of tetrafluoroethylene, perfluoro(lower alkyl vinyl ether) and cyano group-containing (perfluorovinylether) for use in the present invention includes, for example, the one comprising about 45 to about 75% by mole of tetrafluoroethylene, about 50 to about 25% by mole of perfluoro(lower alkyl vinyl ether) and about 0.1 to about 5% by mole of cyano group-containing (perfluorovinylether) as a cross-linking site monomer, sum total being 100% by mole. The terpolymer can further contain various vinyl compounds and fluorinated olefins, as copolymerized to such a degree as not to inhibit the copolymerization reaction or impair the physical properties of vulcanized products.

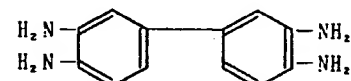
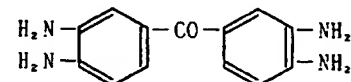
About 0.1 to about 10 parts by weight, preferably about 0.5 to about 5 parts by weight, of at least one of the following compounds is added to 100 parts by weight of the terpolymer as a bis(aminophenyl) compound represented by the following general formula.



[hereinafter referred to as bis(aminophenol)AF]



[hereinafter referred to as bis(aminophenol)]

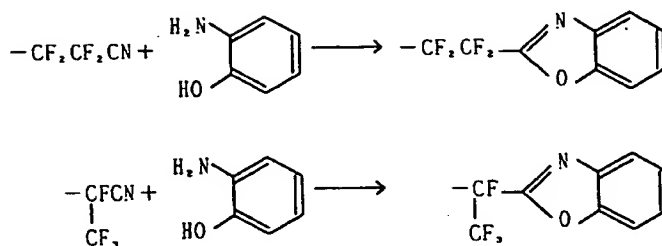


The fluorine-containing elastomer composition comprising the above-mentioned components as essential ones can further contain an inorganic filler such as carbon black, silica, etc., an acid acceptor such as oxide, hydroxide or stearate of a divalent metal, litharge, etc., and other additives, as desired. The composition can be prepared by kneading in rolls, kneader, Bambury mixer, etc. Cross-linking of the composition is carried out by heating at about 100 to about 250°C for about 1 to about 120 minutes. Secondary vulcanization, when desired, is preferably carried out at about 150 to about 280°C for not more than about 30 hours in an inert atmosphere such as a nitrogen atmosphere.

The present inventors disclose in JP-A-6-263952 that a perfluoro(ω -cyanoalkyl vinyl ether) represented by the general formula: $\text{CF}_2=\text{CFO}(\text{CF}_2)_n\text{CN}$ (wherein n : 2-12) is copolymerized as a cross-linking site monomer in place of the cyano group-containing (perfluorovinylether) disclosed in aforementioned JP-A-59-109546 with tetrafluoroethylene, perfluoro(lower alkyl vinyl ether) and a bis(aminophenyl) compound represented by the foregoing general formula is used as a cross-linking agent for the terpolymer.

The nitrile group of the above-mentioned terpolymer is a primary nitrile group, whereas the nitrile group of the present terpolymer is a secondary nitrile group, which has been considered to hardly form an oxazole ring with an o-aminophenol

compound due to the steric hindrance and to be not practical [Journal of Fluorine Chemistry, Vol. 8 Page 295 (1976)].



The secondary nitrile group of the present terpolymer has a higher selectivity to the oxazole ring formation reaction than that of the primary nitrile group and can be attained the improvement of compression set characteristics.

According to the present invention, there is provided a fluorine-containing elastomer composition capable of producing vulcanized rubber products having a good heat resistance and good physical properties with a commercially available, ordinary cross-linking agent free from any safety problem, as contained therein, the composition comprising a cross-linking site monomer which can be readily synthesized with a good selectivity.

PREFERRED EMBODIMENTS OF THE INVENTION

The present invention will be described in detail below, referring to Reference Examples, Examples and Comparative Example.

REFERENCE EXAMPLE 1

4000ml of distilled water, 50g of ammonium perfluoro-octanoate, and 88g of $\text{Na}_2\text{HPO}_4 \cdot 12\text{H}_2\text{O}$ were charged into a stainless steel autoclave having a capacity of 10 liters, and then the autoclave inside gas was replaced with a nitrogen gas. Then, the autoclave was subjected to pressure reduction, and cooled down to about -50°C . Then, 250g of perfluoro (8-cyano-5-methyl-3,6-dioxo-1-nonene) [CNVE], 1660g of perfluoro(methyl vinyl ether) [FMVE] and 560g of tetrafluoroethylene [TFE] were successively charged therein, and then autoclave was heated to 65°C . Then, 500ml of an aqueous solution containing 15g of sodium sulfite and 500ml of an aqueous solution containing 75g of ammonium persulfate were charged therein to start polymerization reaction. 8 hours after the start polymerization reaction, the same amounts of the aqueous sodium sulfite solution and the ammonium persulfate solution as above were charged again therein. After the polymerization reaction was continued for 20 hours, the unreacted gas was purged from the autoclave and the formed aqueous latex was taken out from the autoclave. The latex was salted out with an aqueous 10% sodium chloride solution and dried, whereby 620g of white, rubbery terpolymer A was obtained.

It was found by infrared absorption spectrum analysis that the terpolymer A had a copolymer composition comprising 61.9 mol% of TFE, 37.0 mol% of FMVE and 1.1 mol% of CNVE (characteristic absorption of nitrile group: 2268cm^{-1}).

REFERENCE EXAMPLE 2

The polymerization reaction was conducted in the same manner as in Reference Example 1, except that in Reference Example, 350g of perfluoro(8-cyano-5-methyl-3,6-dioxo-1-octene) [FCVE] was used in place of CNVE, whereby 460g of white, rubbery terpolymer B having a copolymer composition comprising 67.7 mol% of TFE, 30.9 mol% of FMVE and 1.4 mol% of FCVE was obtained.

EP 0 708 140 A1

EXAMPLES 1 and 2

The following components were kneaded in a double roll rubber mill and subjected to primary vulcanization (press vulcanization) at 160°C for 30 minutes and secondary vulcanization at 230°C for 22 hours:

Terpolymer A	100 parts by weight
Bis(aminophenol)AF	1 parts by weight (for Ex. 1)
Bis(aminophenol)	1 parts by weight (for Ex. 2)
MT carbon black	20 parts by weight

The thus obtained vulcanized sheets were subjected to measurement of normal state physical properties according to JIS K-6301, and also to measurement of compression set (by 75% compression of P-24 O-ring) and heat resistance (changes in the normal physical properties after hot ageing at 275°C for 70 hours).

COMPARATIVE EXAMPLE

The following components were kneaded in a double roll rubber mill and subjected to primary vulcanization (press vulcanization) at 190°C for 60 minutes and secondary vulcanization of long duration at 100 to 200°C for 6 hours-200°C for 18 hours-200 to 280°C for 6 hours-280°C for 18 hours.

Terpolymer B	100 parts by weight
Bis(aminophenol)AF	2 parts by weight
Dicyclohexyl-18-Crown-6	0.5 parts by weight
MT carbon black	10 parts by weight
Litharge (PbO)	2 parts by weight

The thus obtained vulcanized sheets was subjected to the same measurement as in Examples 1 and 2.

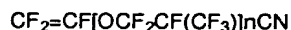
Results of measurement in Examples 1 and 2, and Comparative Example are shown in the following Table.

TABLE

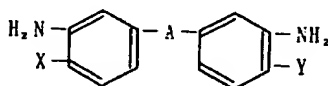
Measurements	Ex. 1	Ex. 2	Comp. Ex.
[Normal state physical properties]			
Hardness (JIS-A)	75	74	77
100% modulus (kg/cm ²)	76	45	71
Tensile strength (kg/cm ²)	179	110	136
Elongation (%)	153	170	140
[Compression set; %]			
200°C for 70 hrs	10	20	39
200°C for 140 hrs	14	29	45
250°C for 70 hrs	13	30	44
275°C for 70 hrs	15	31	49
[Hot ageing test]			
Hardness change (point)	+1	+1	+2
100% modulus change (%)	+4	+4	-4
Tensile strength change (%)	-7	+2	+35
Elongation change (%)	-3	-1	+25

Claims

1. A fluorine-containing elastomer composition, which comprises a terpolymer of tetrafluoroethylene, perfluoro(lower alkyl vinyl ether) and cyano group-containing (perfluorovinylether) represented by the following general formula:



, wherein n is an integer of 1 to 5, and a bis(aminophenyl) compound represented by the following general formula as a cross-linking agent:



, wherein A is an alkylidene group having 1 to 6 carbon atoms, a perfluoroalkylidene group having 1 to 10 carbon atoms, a SO₂ group, an O group, a CO group or a carbon-carbon bond of directly bonded two benzene rings, and X and Y are a hydroxyl group or an amino group.

2. A fluorine-containing elastomer composition according to Claim 1, wherein the terpolymer is one comprising about 45 to about 75% by mole of tetrafluoroethylene, about 50 to about 25% by mole of perfluoro(lower alkyl vinyl ether) and about 0.1 to about 5% by mole of cyano group-containing (perfluorovinylether), sum total being 100% by mole.
3. A fluorine-containing elastomer composition according to Claim 1, wherein about 0.1 to about 10 parts by weight of the bis(aminophenyl) compound is contained as the cross-linking agent per 100 parts by weight of the terpolymer.



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 95 11 6112

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A,D	EP-A-0 606 883 (NIPPON MEKTRON) * page 1, paragraph 2; claims 1-4; example 1 *	1-3	C08K5/18 C08L27/12
A,D	US-A-4 031 124 (DU PONT) * examples 4,5 * -----	1,2	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			C08K
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 17 January 1996	Examiner Engel, S
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document</p> <p>T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document</p>			

EPO FORM 150 (01.91) (P04/01)